

Product/Technology Introduction
Organic Phosphonic Acid

SKIP TEXT

1. Already-existing phosphonic acid

1-1. Unsubstituted phosphonic acid

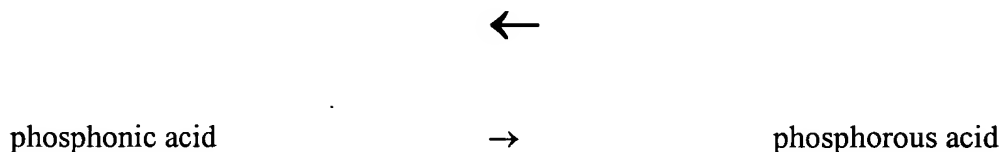
Unsubstituted phosphonic acid is a compound in which two hydroxyl groups are bonded.

Unsubstituted phosphonic acid has a tautomerismic relationship with phosphorous acid.

However, it is thought that the balance of unsubstituted phosphonic acid leans mostly toward phosphonic acid in the vicinity of room temperature in water. Unsubstituted phosphonic acid is a deliquescent crystal, but it is dissolved at 180°C or higher and generates a phosphinic gas.

SKIP TEXT

See the diagrams in the original.



It is thought that the reason why the structure of phosphonic acid is more stable than that of phosphorous acid is that 5 values of a phosphorus atom are thermodynamically stable. 3 values of the phosphorus atom and 2 of 5 values are used, and when 3 values are used, a "d" orbit of the phosphorus atom receives a counter supply from metal and stabilizes a metal atom, which has brought about a very useful knowledge in phosphorus chemistry. For example, the Wittig reaction, the Arbusov reaction, etc. that are often used in organic synthetic reactions mainly use the former effect. The oxo reaction, which is famous in petrochemistry, and ligands such as BINAP catalyst, BisP catalyst, etc. mainly use the latter effect.

1-2. Alkyl phosphonic acid and aryl phosphonic acid

These are compounds shown by the general formula $RP(O)(OH)_2$ or $ArP(O)(OH)_2$.

They are mainly used for rust proofing agents, extracting agents, fixing agents, pH adjusting agents, etc. when manufacturing resin. It is said that the reason why phosphonic acid shows a rust proofing effect is mainly that a steel plate surface is made to be a passive state by phosphonic acid. Recently, by using reactivity of two functional groups of phosphonic acid, it has been used in the fields of reactive flame-resisting agents, and functional materials such as optical materials. A hydroxyl group of phosphonic acid has an extremely high affinity for metal. Furthermore, neutralized salt can be obtained, which easily generates neutralization reaction and reacts. Thus, by using this characteristic, it is used as an extracting agent and a chelate agent, and neutralized salt is used as an additive flame-resisting agent.

See the diagrams in the original. (Page 94)

Alkyl phosphonic acid

Aryl phosphonic acid

In the beginning, phosphonic acid was developed as an extracting agent. Around 1942, based on the Manhattan Project, when there was a need for refining a large amount of uranium and plutonium, as this extracting agent, a glycol system compound (for example, BUTEX, etc.) was originally used. However, these extracting agents had to use a large amount of salting-out agent, which was not practical. In order to solve this problem, upon considering various compounds, TBP (manufactured by Nippon Chemical Industrial Co. Ltd., tributyl phosphate) was found, which does not use other additives at all other than nitrate. This set the stage, and it became known that a phosphorus system compound is appropriate for an extracting agent, and synthesizing of various compounds was tried. In this process, for example, PC 88A (Daihachi Kagaku Kogyo), which is a phosphonic acid ester, was an extracting agent in the spotlight in

those days, in which a separation factor of nickel and cobalt was extremely large. After that, the phosphonic acid ester analogs CYANEX 272 (ACC Corporation), D2EHDA (Daihachi Kagaku Kogyo), etc. were developed. Finally, a phosphonic acid compound became the leading extracting agent.

As described later, in addition to already-existing uses, the number of uses as a functional material has recently increased.

Table 1 shows alkyl and aryl phosphonic acid sold by our company. With respect to alkyl phosphonic acid, products with an ethyl group and an octyl group are sold. Phenyl phosphonic acid and phenyl phosphonic acid dichloride are sold as aryl phosphonic acids. As synthetic materials of alkyl phosphonic acid type, phosphorus trichloride, phosphorus oxychloride, phosphine gas, etc. are considered. Our company has these materials, so it is possible to synthesize various alkyl phosphonic acid types. In addition to the products (Table 1) on the market, we can adjust the products according to the demands from our customers.

See the original for the diagram. (Page 95)

Phenyl phosphonic acid

Table 1 - Alkyl and Aryl Phosphonic Acids

Product Name (Chemical name)	Chemical Formula	Molecular Weight	Boiling Point - Fusing Point (°C)	Chemical Exam Method NO
EPA 70 (Ethyl phosphonic acid 70% solution)	$C_2H_5P(O)(OH)_2$	110.00	bp 60—61 (10 mmHg)	2—1995
Octyl Phosphonic acid	$C_8H_{17}P(O)(OH)_2$	194.21	mp 100-101	2-1995
Phenyl phosphonic acid	$C_6H_5P(O)(OH)_2$	158.09	mp 158-160	3-2524
Phenyl phosphonic acid dichloride	$C_6H_5P(O)Cl_2$	194.99	bp 137-138 (15 mmHg)	3-2611

SKIP TEXT

1-3. Multifunctional phosphonic acids

When synthesizing an additive type flame-resisting agent, the higher the number of hydroxyl groups is, the higher the number of bases can be reacted. Thus, a high flame resisting effect can be obtained. Furthermore, with respect to chelate, as the number of hydroxyl groups increases, the number of metal atoms to be chelated increases. Because of this point, as multifunctional phosphonic acid, our company sells Defloc[?] EH-06 and Defloc NH-05 to be used for the above-mentioned use.

See the original for the diagrams. (Page 96)

Defloc NH-05

Defloc EH-06

Table 2 - Multifunctional Phosphonic Acid

Product Name (Chemical name)	Chemical Formula	Molecular Weight	Fusing Point (°C)	Chemical Exam Method NO
Defloc [?] EHO6 Hydroxyl ethanediphosphonic acid (HEDP 60% solution)	$C_2H_8P_2O_7$	206.03	-40	2-2936
Defloc [?] NH05 Nitrilotris methylene phosphonic acid (NTP 50% solution)	$C_3H_{12}P_3O_9$	299.05	-10	2-1866

Additionally, as an additive flame-resisting agent using Defloc, HISHIGARD[?] select series are manufactured to be sold mainly for electronic materials. As an example, the structure of HISHIGARD select 6ME is shown. In general, it is known that a phosphorus system flame-resisting agent shows an excellent flame resisting effect when used in combination with a nitrogen system compound. HISHIGARD select 6ME meets these purposes since P and N are appropriately included in the molecules.

See the original for the diagram. (Page 96)

HISHIGARD select 6ME

In our company as well, the chelate amount of Defloc with respect to various metal ions is measured. In particular, the chelate force for an iron ion is the EDTA value or higher and is used as a scale suppressing agent in factory circulation water, etc.

Table 3 - Iron Chelate Amount of Defloc (mg/mg)

	NH-05	EH-06	EDTA
pH 2	131	187	169
pH 5	122	222	153
pH 10	456	679	185

2. Developed product phosphonic acid

SKIP TEXT

2-1. Acyl phosphonic acid

This is a compound shown by the general formula $RC(O)P(O)(OR)_2$ and is different from ordinary phosphonic acid. It shows a characteristic in which P-C bonding is easily opened and split. It is often observed that a stretching vibration peak of a carbonyl group by an IR spectrum is $1640-1670\text{ cm}^{-1}$. This suggests that $C=O$ group and $P=O$ are conjugate. It is said that this is related to the open/split mechanism of P-C bonding.

As a use of acyl phosphonic acid, use as a photo polymerization initiator is considered. Acyl phosphonic acid has been variously proposed as a photo initiating mechanism. When it is photo-irradiated to acyl phosphonic acid of tertiary alcohol in benzene, in P-C bonding, a compound is obtained into which an alkyl group of ester is inserted. Thus, this is considered as polymerization initiation by radical open/split of P-C bonding.

See the original for the diagram. (Page 97)

2-2. Amino phosphonic acid

This is a compound shown by the general formula $\text{H}_2\text{NRP}(\text{O})(\text{OH})_2$. It is known that more than 30 types of C-P compounds are included as a vital substance. These compounds are roughly classified as phosphonic acid systems and phosphine acid systems. It is clarified that any of these is generated by using 3-phosphono pyruvic acid as a precursor. Functions of these compounds in a living body are not yet analyzed. However, in an aerobic protozoa tetrahymena, a large amount [of these compounds] is included in a surface film and a woven hair film. Thus, it is considered that they function as a protective substance such as a cell wall of bacteria. Furthermore, they are also included in cohesion bile acid of an anaerobic [illegible] protozoa, so it is assumed that for these living creatures, they function in a digesting process. Additionally, it is known that spiral shell types, bivalve types, and cephalopods, which are mollusks, are reservoirs of a P-C compound beginning with amino phosphonic acid.

SKIP TEXT

Nippon Chemical Industrial Co. Ltd.